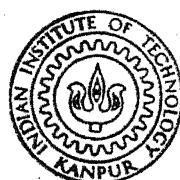


SELF-QUENCHING OF FLUORESCENCE OF IODINE

BY
VEDA NAND SAH

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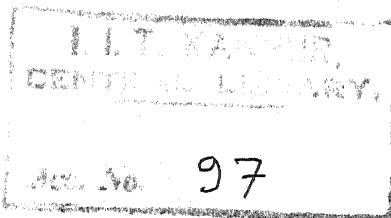
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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
JUNE, 1968

SELF-QUENCHING OF FLUORESCENCE OF IODINE

A Thesis Submitted
In Partial Fulfilment of the Requirements
For the Degree of
MASTER OF TECHNOLOGY IN CHEMICAL ENGINEERING



by ..

VEDA N AND SAH

to the ..

✓CHE- 1868-M-SAH-SEL

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY-KHARAGPUR

JUNE, 1968.

A_C_K_N_O_W_L_E_D_G_E_M_E_N_T_S

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I_N_T_R_O_D_U_C_T_I_O_N

Fluorescence is generally defined as a luminescence emission that is caused by the flow of some form of energy into the emitting body, this emission ceasing abruptly when the exciting energy is shut off. Another basis frequently used for characterizing luminescence is its persistence after the exciting source is removed. Certain substances continue to emit light for extended periods after the exciting energy is shut off. This delayed emission or after glow is generally called "Phosphorescence". The term fluorescence being reserved for the light emitted during the period of excitation. The difference between fluorescence and phosphorescence lies entirely in the time lag involved in the reemission of the light after the exciting source has been removed with fluorescence, emission of the light by the substance ceases immediately when the energizing radiation is extinguished. For this case the duration of the afterglow has been found by a number of investigators to be of the order of 10^{-6} seconds. A phosphorescent material on the other hand continues to emit light for a period of time after the energising source has been removed. The duration of the afterglow varies with the substance and may be anything from 10^{-2} seconds to several days.

The process that occur in luminescence may be most simply illustrated in the case of an isolated atom. The atom can exist only in certain states of energy, corresponding to certain possible different configurations of its electrons. It can make a transition from one electronic state to another only if it simultaneously absorbs or emits a precise amount of

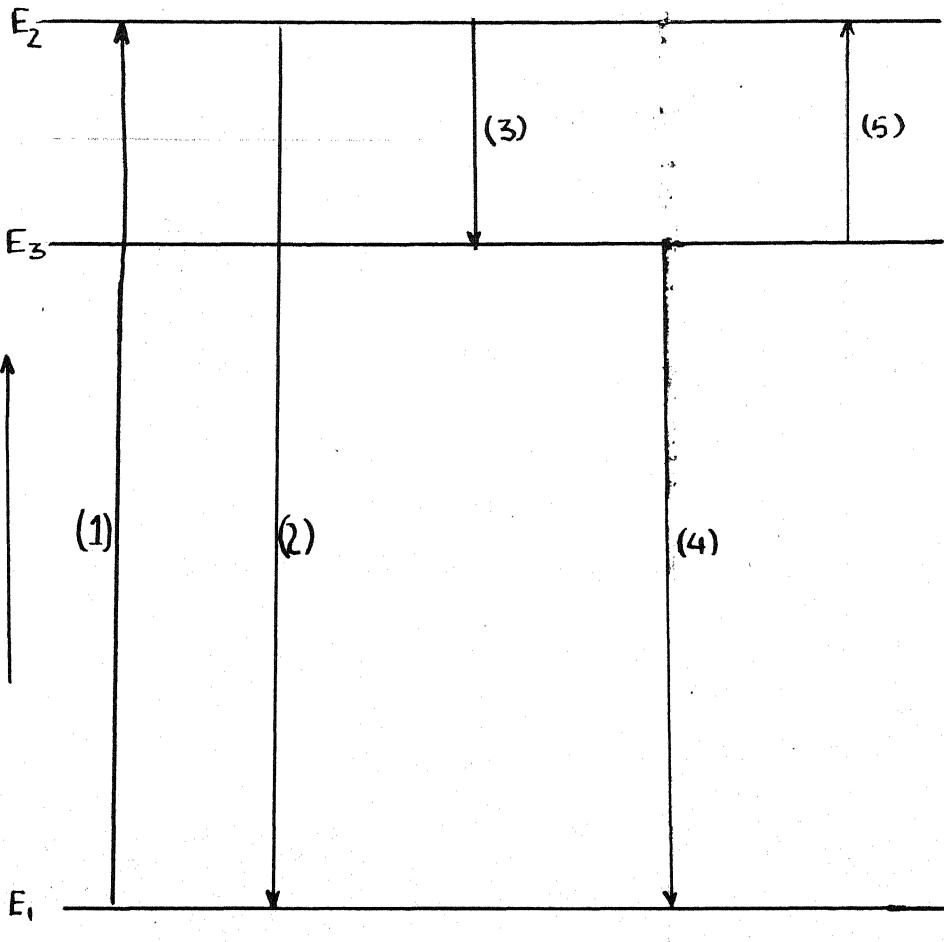


FIG. - 1.

Schematic representation of energy levels and electronic transitions in an atom. E_1 = ground state, E_2 = Excited state
 (1) = Excitation (2) = emission of resonance luminescence
 (3) = radiationless transition to lower excited state (4) = luminescence emission, if transition $E_3 \rightarrow E_1$ is allowed if it is not allowed (4) does not occur and E_3 is called a metastable state (5) = Stimulation of atom back to emitting state.

energy. ΔE , equal to the difference in the energy of the initial and final states of the atom. The accompanying figure 1 shows schematically three such energy levels of an atom, the level of lowest energy, E_1 , representing the atom in its normal 'ground State' or 'unexcited' state. The levels of higher energy E_2 and E_3 represent electronically 'excited states' of the atom, corresponding to different orbital motions of one of its electrons around the atomic nucleus.

The excitation of the atom from state E_1 to state E_2 requires the absorption of an amount of energy $\Delta E = E_2 - E_1$. If this excitation is to be produced by absorption of light, the exciting light must have a wave length, given by the relation,

$$\text{abs.} = \frac{hc}{\Delta E}$$

where h is Planck's constant and c is the velocity of light.

The excited atom can dissipate its extra energy in a number of ways; for example, by transferring its energy to another atom on collision with it. If this happens, the excited atom returns to the ground state without emitting radiation. If, however, no process occurs to dissipate the extra energy of the atom, it will eventually return to the ground state spontaneously with the liberation of the excess energy as luminescence. The emitted light will again correspond in energy to

ΔE and will have a wavelength λ (emitted) $= hc/\Delta E$, identical with the wave length of the absorbed light. In this case the luminescence is called resonance radiation. If a transition between the atomic energy levels involved is highly probable

(a so-called "permitted" or "allowed" transition) the time the atom spends in the excited state is very small of the order of a hundredth of a microsecond for transitions involving light in the visible spectrum. It may happen that by some process other than by light emission, such as by a collision with another atom, the excited atom loses some energy and assumes an energy state E_3 , of intermediate energy between E_1 and E_2 . If the transition from state E_3 to state E_1 likewise has a high probability, luminescence will occur with a wavelength λ (emitted) = $h c / (E_3 - E_1)$. Since $E_3 - E_1$ is smaller than $(E_2 - E_1)$, the luminescence in this case will be of longer wavelength than the resonance radiation.

If, however, direct transition between state E_3 and state E_1 is highly improbable (a so-called "forbidden transition") state E_3 is known as a "metastable" state. The atom can remain in this excited state for longer periods of time, and while it does so, no emission takes place. If, by a collision or by some other process, the atom regains the energy $(E_2 - E_3)$ it is returned to the excited state E_2 , from which transitions to the ground state is permitted and luminescence corresponding to $(E_2 - E_1)$ is again emitted.

The existence of metastable states like E_3 is the origin of delayed emission or phosphorescence previously discussed. The atom may spend a long time in such a state before some external influence returns it to an emitting state like E_2 , in which case the luminescence is correspondingly delayed and appear as an afterglow. In order for the atom to get from E_3 to E_2 , energy

must be absorbed somehow, say by collision with other atoms. The higher the temperature the greater is the probability of such a collision and the consequent return of the atom to an emitting state. The duration of the afterglow will therefore depend very strongly on temperature. At elevated temperatures the atoms will be excited more rapidly back into the emitting state and there will be a bright afterglow of short duration. At lower temperatures, the atoms will be raised back to the emitting state very slowly and the afterglow will be of long duration but of low intensity. At sufficiently low temperatures the return to an emitting state is practically completely prevented and the excess energy is frozen in the atom. This criterion is the basis for a meaningful definition of phosphorescence. Phosphorescence is therefore a luminescent afterglow whose duration is dependent on temperature. If an afterglow is observable, but its duration does not depend upon the temperature of the emitter, the emission is a fluorescence. "Thermo luminescence" is the release of "frozen-in" energy by warming a previously excited luminescent body. The atom may be lifted out of metastable state by absorption of a photon of energy $h c / (E_2 - E_1)$, in which case the process is called a "stimulated" emission. In either case, once the stored-up energy is released as luminescence, the body ceases to emit light, unless it is once again exposed to exciting radiation.

The principle illustrated in the above discussion may be extended with little modification to the case where the primary absorption or excitation act completely removes an electron from an atom (ionizes it), instead of merely raising it to an excited state. Of course, for a given species of atom

a more energetic quantum is necessary to ionize the atom, than to excite it. Once the electron is free, it can be trapped temporarily on other atoms and its return to the parent atom can also be delayed by this mechanism.

Generally, fluorescence is produced by excitation of a substance with light of short wavelength which is absorbed and converted to an emitting radiation of longer wavelength. This follows the classical formula of Stokes. Hence the fluorescence efficiency which is the ratio of a light emitted in fluorescence to the amount absorbed, is always less than unity. There may be exceptions to Stoke's law. When the atom or molecule possesses energy of vibration at the time of its excitation to a higher energy state, the return transition carrying it to a lower state than the original one resulting in the emission of a frequency higher than that of the exciting radiation.

✓ This project is part of an attempt to study the optical and photochemical properties of Iodine. Intensity of fluorescence of iodine vapor filled in the cell under different temperatures from 0°C to 30°C has been measured. The self quenching constants of iodine fluorescence has been measured, the value agrees closely with the one reported in the literature (3, 4, 5, 6, 9). From the self quenching constant, the other kinetic parameters like collision cross-section and photo-chemical reaction rate constant have been calculated. ✓

HISTORICAL DEVELOPMENT

Fluorescence of iodine excited by the green line of mercury at 5461 Å was first observed by Wood⁽¹⁾ and Frank and Wood⁽²⁾. The spectrum of iodine excited by 5461 Å line consists of a series of bands stretching from 5461 Å towards the red. On excitation with narrow green line (Hg-5461 Å) the iodine molecules are raised to the 26th vibrational level ($v_{a,b}$) of $^3\text{O}^+u$ state and fluorescence bands are produced by transitions back to ground state $26' \longrightarrow 0''$, $26' \longrightarrow 1''$, $26' \longrightarrow 2''$, $26' \longrightarrow 3''$ etc. The resonance spectrum has been extended as far as the 39th member at 9097 Å. The complete resonance spectrum of Iodine vapor excited by the green line of mercury 5461 Å from $26' \longrightarrow 0''$ to $26' \longrightarrow 39$ has been given by Pringsheim⁽⁷⁾. The band under these conditions have only a doublet structure (1_e).

The quantitative measurements of this effect yielded the values of inelastic scattering cross-sections for the excited state involved. This type of measurements were carried out by Polanyi⁽³⁾ and Arnot and McDowell^(4, 5). They presented the results which conflict with that of the earlier workers.

A major advance in technique was made by Brown⁽⁶⁾ when he observed the fluorescence photoelectrically under improved resolution. He used sodium D lines as an excitation source in order to investigate energy transfer in a vibrational state other than the one previous studied. The results showed marked improvement over previous work. However, it became clear that measurements have to be repeated in order to form a valid basis

for comparison. The aim of the present work is to compare the self quenching constants with the previous work (3, 4, 6). It is also intended to calculate reliable quenching cross-sections in the measured quenching constants and the radiative life time of excited iodine as given in reference 8 and 9.

THEORY OF THE FLUORESCENCE OF IODINE

Iodine vapor at room temperature is in the form of molecular state in an evacuated glass tube containing a few small fractions of the element. It fluoresces brightly when illuminated by white light.

Under monochromatic excitation the absorption spectrum yields resonance spectra. Energy levels of iodine molecule resonance spectra excited by the green mercury line 5461 and the two yellow lines 5770 has been shown in Fig. 2.

The band spectrum of iodine was photographed with a grating spectrograph of 40ft. focus. Nearly 120 lines were counted in a spectral region equal to the distance between the yellow lines of sodium. Showing that the total number in the entire spectrum between the green line and the extreme red was more than 36000, which was explained by Lenz⁽¹²⁾, Mecke & Kratzer⁽¹³⁾ and Leomis⁽¹⁴⁾. A system of energy levels can be constructed for the case of these molecules similar to those given in Fig. 1. For the resonance fluorescence of an atom, except the vibrational energy is added to that of electronic excitation.

Fig. 2 shows the such set of levels, the lower or the ground state ϵ' for the molecule before and the upper or excited state ϵ'' after the impact. Each of these states is subdivided into vibrational levels which crowd together as their quantum numbers V'' , 0, 1, 2, 3 etc. increases. These levels are subdivided into rotational levels which have not been shown in the figure. The transitions which occur with three different absorption and

emission processes are indicated by upward and downward arrows respectively as before and quantum numbers of the vibrational levels of the two electronic states are indicated, at the right, each fifth line only being shown.

Consider a molecule on the σ level of the ground state and without vibration. The absorption light corresponding to the 5461 mercury line i.e. 18311 cm^{-1} raises the molecules to the 26th vibrational level of the upper state as indicated by the upward arrow at the left, the change in electron configuration having liberated a force sufficient to give the atoms 26 quanta of vibrational energy. The return of the molecules from this excited state to the lower state ϵ'' can take place from the upper vibrational level to any one of the lower. This means that if there are large number of molecules excited to the same upper level of the ϵ' state, as will be the case with illumination by strictly monochromatic light, the number of lines recorded in the fluorescence spectrum will indicate the number of vibrational levels utilized in the lower or ϵ'' state after excitation. The transitions are indicated by the adjacent downward pointing group of arrows corresponding to the series of lines of decreasing wave number of increasing wave length which constitute the resonance spectrum. It is also clear that after the return of the electrons to the normal state, the molecules, which were initially without vibration have been left with various amounts of vibrational energy, those which have emitted the light of longest wavelength i.e. shortest wave numbers, being left with the largest amplitude of vibration. This vibrational energy is rapidly spent in warming the vapor i.e. increasing the velocity of the

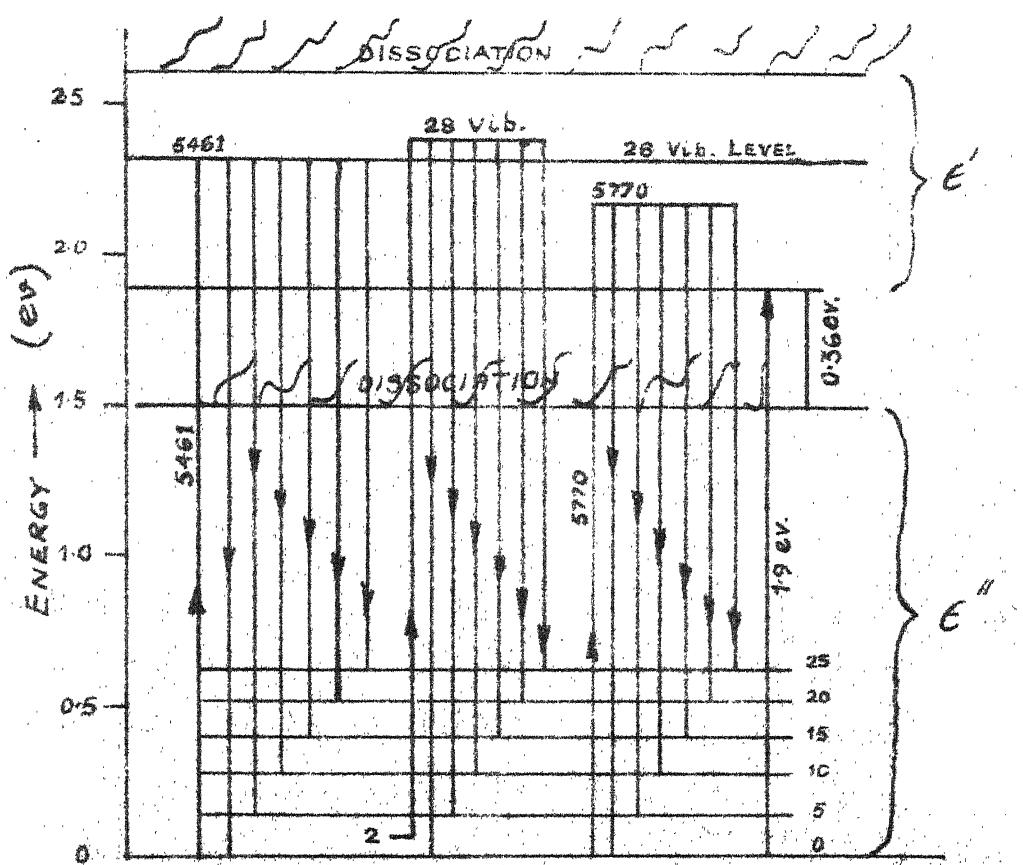


FIG -2 ENERGY LEVELS OF IODINE MOLECULE
Resonance Spectra.

rebound of molecules, when in collision.

If the vapor is at a higher temperature, a large number of vibration to start with. The transitions in this case are shown by second group of arrows, the one representing the absorption based on the second vibration level and ending on the 28th. The return arrows ending on levels, 0, and 1 represent spectrum lines of shorter wavelength, than that of the exciting light, or anti-Stokes lines. Increasing the temperature increases the number of these lines as the molecules are on still higher vibrational levels to start with.

The transitions involved in the case of excitation by light of yellow line 5770 is shown by the third set of arrows. Absorption takes place as before from the 0 level of the ground state, but, the energy of the photon is only sufficient to excite the molecule to lower vibrational level, from which transitions back to all of the levels in the ground state occur. The lower wave number of the exciting radiation is indicated by the left hand arrows, while the others represent the numerous fluorescent lines.

If a foreign gas is mixed with the iodine vapor, the collisions between the foreign gas and iodine molecules alter the amplitude of the vibrations of the latter, throwing them to various neighbouring energy levels, which have not been shown in figure3. The result being that emission lines in increasing number appear as the foreign gas pressure is raised, until eventually a large part of the complete band spectrum is recorded.

Iodine molecules is formed of two atoms held together by a force which changes from attraction to repulsion as the distance between the nuclei diminishes and for a certain inter nuclear distance no force operates and the atoms are in equilibrium.

If now the molecule is struck by a photon of light of suitable energy, the photon disappears, giving up its energy to the molecule, which is thrown into an excited state. In this condition the equilibrium distance between the nuclei is greater i.e. the repulsive part of the force comes into play, which starts to-and-fro vibration. During the vibration the potential energy of the molecular takes on values corresponding to the momentary distance between the nuclei. The processes involved in this and subsequent events involving fluorescence can best be shown by potential curves.

The electronic states and potential diagram of the iodine molecule have been very well explained by Mathiesen and Rees⁽¹¹⁾. The spectroscopic data on the iodine molecule have been analysed; The potential energy diagram computed for some ten electronic states up to 55000 cm^{-1} has been shown in figure 4.

Here to explain the fluorescence phenomenon of iodine, two levels, ground state (X) and excited state (B) has been taken into consideration. Fig. 4.

Potential Curves and the Franck -Condon Principle 1

In Fig. 4, the ground state (X) and excited state (B) correspond to the two state ϵ^+ and ϵ^* state in Fig. 2. Both

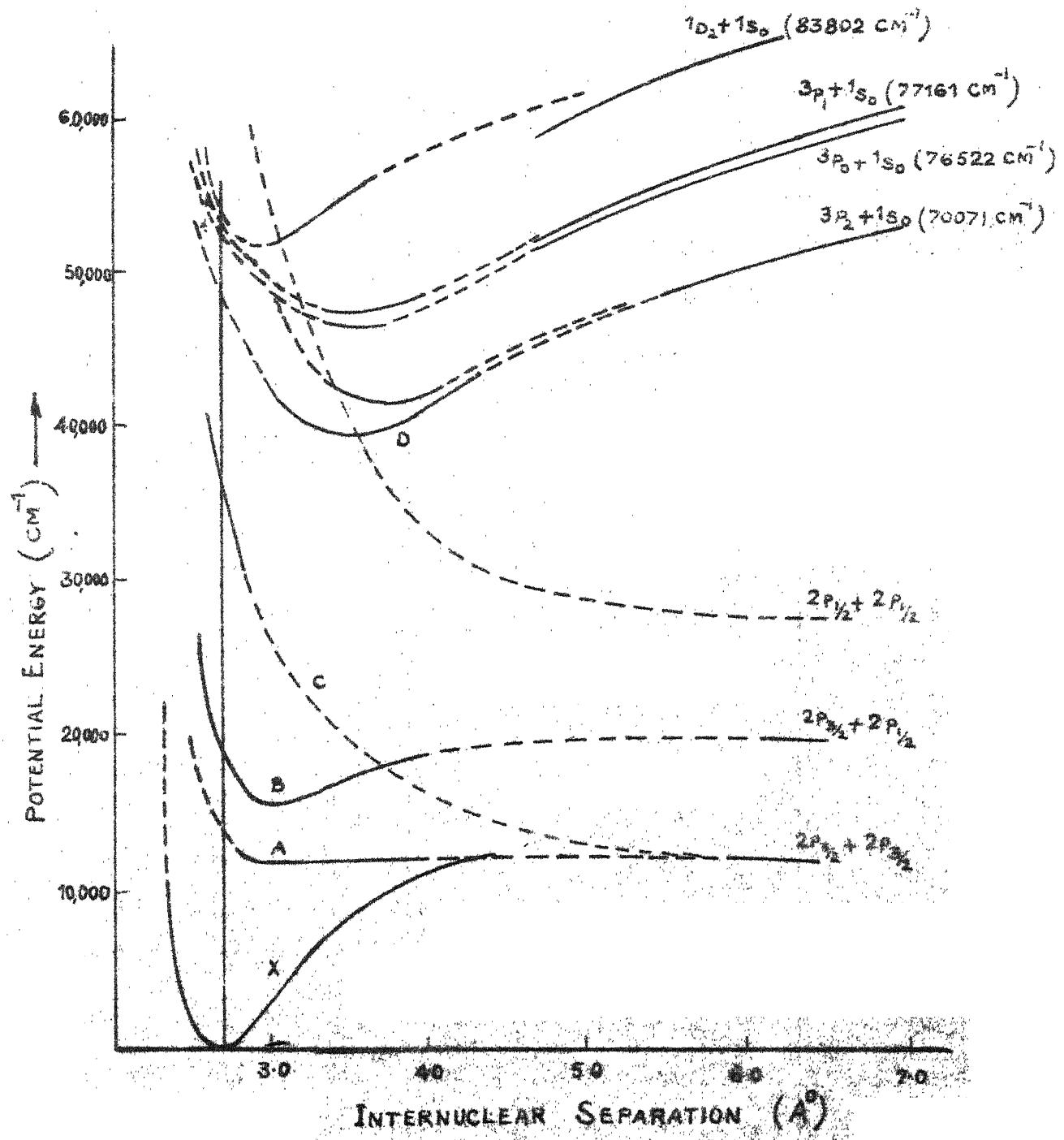


FIG-3. POTENTIAL ENERGY DIAGRAM for IODINE MOLECULE

are divided into horizontal vibrational levels as before and both of the right hand branches approach asymptotically a level at which the vibration amplitude becomes so great that the molecule dissociates into two atoms. The height of this level on the scale gives the work that must be done to cause dissociation. Vibrations of the lower state can be excited only by heat, while those in the upper state result from the force of repulsion between the atoms when the electronic configuration is altered by the impact of a photon.

Since only relative motion between the two atoms need be considered, one of the atoms can be regarded at rest on the axis of ordinates, and other moving toward and away from it along a line parallel to the axis of abscissae. In Fig. 4, the moving atom will be assumed as the one excited by the photon and will be designated by letters in its various positions on the line of vibration, while the stationary atom remains on the axis of ordinates, which is not shown in the figure but lies to the left of the scale. The internuclear distance r for any position of the molecule on the curve is indicated by the point immediately below it on the abscissa (scale in centimetres $\times 10^{-8}$ Å).

In the present case the atom MA is represented at the equilibrium position of the molecule on the lowest or zero level at distance $r = 2.6\text{\AA}^*$ from the stationary atom. When struck by a photon of energy corresponding to a quantum of the green mercury line, radiation 1831 cm^{-1} and represented by the length of the arrow MW, no immediate change in the interatomic distance occurs,

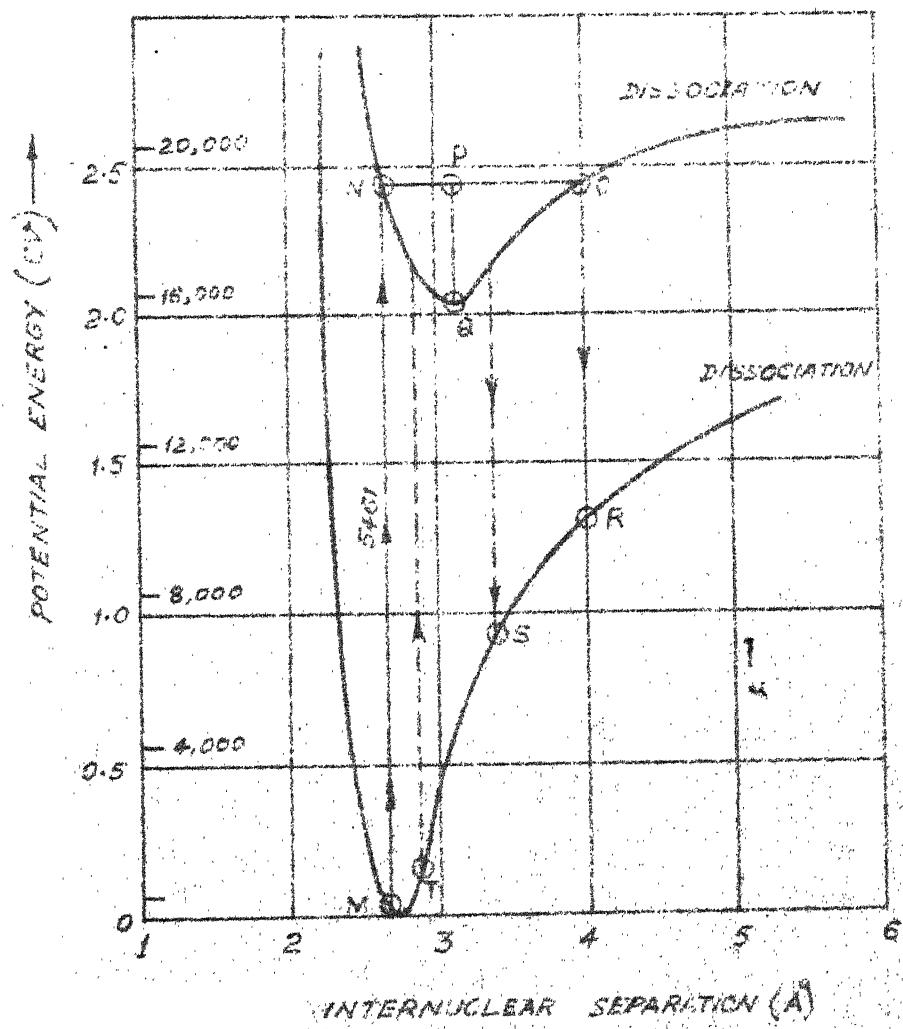


FIG. 4 - POTENTIAL CURVES FOR IODINE MOLECULES.

since by the Franck-Condon principle, the electronic jump in the atom N takes place so rapidly in comparison with the vibrational motion, that the internuclear distance has not time to change during the electronic transition.

The molecule is on the upper curve with the same internuclear distance as before, but the repulsive part of the force now comes into play as a result of the change in the electronic configuration of the atom, and a to-and-fro vibration of the atom between N and O results. At N and O the energy is wholly potential, while at intermediate points it is divided between potential and kinetic, the latter having its maximum value at P where it is represented by the length of the dotted line PQ, Q being the equilibrium position on the upper curve at which point the internuclear distance is $r = 3 \text{ \AA}'$ instead of 2.6 \AA as on the lower curve. The height of Q above the base line is the measure of the electronic energy of the molecule.

Transitions up and down from the upper to lower curve will be more frequent in the intermediate vicinity of N and O where the atom is at rest, spending more time here than in the intervening region which it traverses at high velocity. The downward transitions from the 26th vibrational level to the levels 0 - 35 of the lower state, gave rise to a series of 35 double lines, some members being very faint or missing entirely. These restrictions to certain levels can be explained only by employing the methods of wave mechanics.

In treating the problem from the viewpoint of potential

curves, the restrictions to certain vibration levels of the lower state, from a given level in the upper state, can be shown by the application of Franck-Condon principle, which specifies that the lines of the greatest intensity will be those for transitions in which no change in the position and velocity of the moving atoms occurs. The impact of a photon of green light on the atom at A, the equilibrium position of the lower curve, raises it to N on the upper curve exciting a vibration between N and O at which points the potential energies are equal, in other words the line NO can be regarded as the upper level. The transition from O to R corresponds to an emission of a quantum of infra-red light of wave number 8460 or $\lambda = 1.2\mu$, given by the length of the line OR as measured up from zero on the scale to the left. This should be the brightest line in this region by the Franck-Condon principle. Transitions to levels above and below and above N involves changes of position and velocity of the atom of increasing amount and, in consequence, of diminishing intensity. The same effect will be found for transitions from N, the return to N leaving the molecule in its initial state on zero level. Lines resulting from transitions to higher levels of the ground state show diminishing intensity. Anti-Stokes lines cannot occur in this case.

There are thus two widely separated regions of the spectrum in which lines of higher intensities occur, for cases in which the excitation is at the short wave length of spectrum, both lying on what is known as the condon-parabola. These two

regions approach if we excite by light of increasing wavelength as we can see from the case of transitions shown by dotted lines, point S and T lying nearer the vertex of the parabola. Should the unlikely transition occur when the atom is at P, having at this point maximum kinetic energy P_0 , we have emission resulting from a transition from Q on the upper curve to levels in the neighbourhood of U on the lower one. These will give very faint lines in the regions between those of maximum intensity.

Fluorescence Quenching:

The quenching of fluorescence by foreign gases and by I_2 itself undoubtedly occurs by induced predissociation. Turner⁽¹⁶⁾ has detected I_p atoms in a mixture of I_2 and A_p illuminated with light of frequency in the banded portion of the absorptive spectrum by absorption of atomic I resonance lines Rabinowitch and Wood⁽¹⁵⁾ found a quantum yield of unity, for this process by measuring the decrease in molecular extinction of I_2 vapor on illumination in the presence of foreign gases. Thus at the pressures used each excited molecule was dissociated by collisions. If this evidence for an induced predissociation mechanism is accepted, the question arises as to what repulsive state or states are involved.

Quenching of fluorescence may be observed by magnetic field, which has been shown by Turner⁽¹⁶⁾. Quenching of fluorescence has been explained by Mulliken⁽¹⁷⁾, Matheson and Rees⁽¹⁸⁾ and Zener⁽¹⁹⁾.

It has not been possible to measure the quenching from only

one vibrational level, since vibrational transfer rates with most foreign gases are of the same magnitude as quenching rates. Fluorescence appears from levels other than the initial one. Although there is no reason to expect the same quenching rate for all vibrational levels, it may not differ much over small ranges of the vibrational quantum number. An estimate, at least of the quenching from the level initially populated can be obtained by observing the effect of foreign gases on the total fluorescence from $B^3\Pi_{0+}$. In the case of self quenching, it is possible to measure the quenching from a single vibrational level since no vibrational transfer was observed even at high I_2 pressures.

SELF-QUENCHING :

Self-quenching efficiency can be examined by measuring the intensity of a single fluorescence line as a function of I_2 concentration or by observing the fluorescence over a wide frequency range directly with the photomultiplier. The latter technique was used to find the self-quenching by Brown and Klemperer (6).

In the absence of foreign gases the steady state rate of formation of the excited molecules can be equated to the sum of the rate at which they return to the ground state by fluorescence, and the rate at which they are dissociated through collisions with neighbouring I_2 molecules. The expression given by Brown & Klemperer is as follows :

$$\Sigma k_a [M] = [M^*] \tau^{-1} + k_s [M] [M^*] \quad (1)$$

where k_a is a rate constant representing the excitation process, and depends on the ϕ lamp intensity, cell geometry, etc., $[M]$ is the total concentration of ground-state molecules and is proportional to the concentration of the actual state or states absorbing the excitation radiation; τ is the radioactive life time of excited state, $[M^*]$ is the concentration of excited vibration-rotation state; and k_s is the rate constant for self-quenching. The light intensity I can be measured with the help of photomultiplier and can be related to $[M^*]$ where I is proportional to $[M^*]$.

Foreign - Gas - Quenching :

In foreign gas quenching the steady state rate of excitation can be equated to the sum of the rate of fluorescence, the rate of self-quenching and the rate of foreign-gas quenching, giving the equation

$$k_a[M] = [M^*] \tau^{-1} + k_s[M][M^*] + k_q[X][M^*] \quad \dots \quad (2)$$

where k_q is the rate constant for foreign-gas quenching and (X) is the foreign gas concentration.

Collision Cross-Section :

On the basis of kinetic theory k_q (or k_s) may be related to a collision cross-section (or) by equation

$$k_q (\text{or } k_s) = \sigma_1^2 \left(\frac{8\pi RT}{\mu} \right)^{1/2} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \quad \dots \quad (3)$$

where R is the gas constant (ergs per degree mole), T is the absolute temperature and the reduced mass of the colliding particles (g/mole).

EXPERIMENTAL SET - UP

1. FLUORESCENCE CELL AND IODINE CONTAINER :

Fluorescence cell consisted of a pyrex tube 30 mm. in diameter and 120 mm. long with a optically flat glass window of 1/16" thick sealed at one end. The other end of the cell was closed except for a gas inlet tube of 12 mm. diameter with proper stop-cock (*) and ground glass joint (**) to evacuate the cell.

One side tube of 6 mm. diameter normal to the inlet tube was connected to a male part of a ground-glass joint of B-10 size having one stop-cock of 2mm. size in between. The B-10 size ground glass joint had been provided to connect the iodine bulb with the help of a female part of the ground glass joint of B-10 size having one 2mm. stop-cock in between the ground-glass joint and the bulb such that the cell and remaining part upto the stop-cock in the bulb can be evacuated isolating the bulb containing iodine flakes.

5 cm. of the centre portion of the bulb was illuminated with a focussed beam of monochromatic radiation, 2cm. in width.

(*) The stop-cocks were supplied by Corning Glass Works, Corning, New York.

(**) All the ground glass joints were supplied by Quickfit & Quarts Ltd.

" Quickfit " Works, Heart of Stone
Staffordshire, England.

2. EXCITING SOURCE :

The PEK type 202 Mercury short Arc Lamp was used to excite the fluorescence. The lamp was housed according to the instruction given by the H-701, 2372 instruction manual and power supplied to the lamp by PEK Model 701 which was operated at 117/118V 60 through a constant voltage regulating transformer.

3. INTERFERENCE FILTER :

The monochromatic light of 5461 Å was obtained by using the interference filter of No.566 of OPTICS TECHNOLOGY INC. to excite the fluorescence of iodine. The wave length of the fluorescence light ranges from 5461 Å to 12200 Å approximately but the maximum probability of the emission wave length is about 7000 Å. Hence the interference filter of No.700 of OPTICS TECHNOLOGY INC. was used to transmit the fluorescence light.

4. LENS AND SLITS :

A 3" diameter and 8" focal length of quartz plane-convex lens from INDUSTRIAL OPTICS CORP. was used to render the exciting beam parallel.

Two slits having opening 5 cms. X 2 cms. were used to cut off diffuse light from falling on the cell.

5. PHOTOVOLT MULTIPLIER PHOTOMETER :

Photovolt line operated super sensitive electronic Multiplier Photometer series 520-M supplied by "Photovolt Corporation" was used to measure the intensity of fluorescent light. It consists of a main unit and a search unit. This Photovolt Multiplier

Photometer operates with electronic amplification and use an electron multiplier tube as the light sensing element. The photo-multiplier tube converts light falling on its cathode into an electron current which is then successively multiplied within the tube by secondary emission at each of a number of additional dynodes and finally collected by the anode.

Main Unit :

The main unit contains the amplifier, the indicating meter the power supply and control. The indicating meter has four range positions, marked X1000, X100, X10 and X1. Position X1 is the most sensible range. Fullscale deflection on this range corresponds to 0.01 microlumen.

The sensitivity of the needle deflection can be controlled by about 40%.

Search Unit :

It houses the multiplier tube, having one window of 1" diameter in the house.

6. HOUSING OF THE SEARCH UNIT AND THE CELL :

The search unit and fluorescence cell was housed in a wooden box, which was painted black inside. The search unit was clamped horizontally keeping the opening of the search unit up. The fluorescence cell was clamped vertically and the flat window facing towards the search unit window. The filter No.700 was placed on the search unit to transmit the light from 6900 Å to 7200 Å and maximum transmission on 6900 Å.

2. OPTICAL ARRANGEMENT TO EXCITE FLUORESCENCE AND TO MEASURE THE INTENSITY OF FLUORESCENCE :

The PEK Type 202 Mercury Short Arc Lamp, Interference filters, lens, slit, fluorescence cell, search unit and a box to keep the search unit and fluorescence cell in dark were rigidly mounted on an optical bench (Cenco) such that the parallel beam of monochromatic light of 5461 \AA excited the iodine vapor to B-state.

First the fluorescence cell was evacuated by connecting the cell to the vacuum system with the help of ground glass joints which had been provided for this purpose. Then the iodine bulb was connected to the cell keeping the stop-cock of the bulb closed so that iodine vapor was prevented to go to the cell and the vacuum system. The iodine was supplied by Sarabhai Merck Ltd. Wadi, Baroda. Purity stated to be more than 99%. It was resublimated twice.

When the vacuum in cell and the system becomes less than a micron liquid nitrogen in a dewar flask was kept under the trap in between the cell and the manometer so that no vapors of iodine could be allowed to go into the system and manometer. The temperature of the iodine bulb was kept constant for particular run. The vacuum in the system was seen with the help of thermocouple gauge tube Cat. STC-004, Consolidated Vacuum Corporation. The iodine bulb was kept at different temperatures from 0°C . to 50°C . to control the iodine vapor pressure. A beaker with inlet and outlet water facility was kept below the iodine bulb. Water at a known temperature was circulated

through this beaker so as to flow past the iodine bulb. The constant temperature water was supplied by a thermostat. A thermometer was suspended in the beaker to measure the correct temperature of the water. The iodine flakes in the bulb was allowed to stay in contact with the water for at least one and half hour before taking the iodine vapors into the cell.

The vapor pressure at different temperatures were obtained from the thermodynamic data of Gillespie and Fraser⁽²¹⁾. Appendix 1 shows the normal vapor pressure of crystalline iodine corresponding to temperature ranging from 0°C. to 114.15°C., the melting point of the iodine crystal.

INTENSITY MEASUREMENT :

The cell was filled with iodine vapor at a certain temperature. The stop cocks of the cell were closed. The cell was detached from the vacuum system and clamped in its position on the optical bench. The clamping arrangement was such that it was vertical and identical position whenever it was kept in the box. After keeping the cell in its proper position the source lamp was started. Monochromatic radiation of 5461 Å was used for excitation of fluorescence. The fluorescent light passing through monopass filter which has a cut off upto 6300 Å and transmission from 6300 Å to 7300 Å was collected by the search unit and the meter readings were taken on the indicator.

Table 1 shows the intensity of fluorescent light for different concentrations. The concentrations of iodine was calculated using ideal gas law at low pressure.

THE VACUUM SYSTEM :

The vacuum system consisted of a mechanical pump, a silicon oil diffusion pump and a trap to prevent the silicon oil to go into mechanical pump. There were two more traps in between the diffusion pump and a mercury glass manometer. Two 10mm. size high vacuum stop-cocks were used to isolate the diffusion pump. One male part of a ground glass joint of size B-14 was connected to the system after the manometer. There was one stop-cock in between the ground glass joint and the manometer. A thermocouple gauge to measure pressures of the vacuum system and the cell upto a micron was included in the vacuum system after the manometer. A liquid nitrogen trap prevented the iodine vapor to come in contact with the manometer and the pumps etc. Two stop-cocks were used to vent the system isolating the diffusion pump.

RESULTS

KINETIC SCHEME :

When viewed as a simple photochemical system, the system studied in these experiments is composed of ground state iodine molecules, excited iodine molecules free iodine atoms, and radiation in absence of foreign gas molecules. The photo-chemical processes that can take place are as follows :

Activation :



Fluorescence :



and it can be written

$$\sum_n k_{Fn} = k_F \quad \dots (6)$$

Self quenching :



The scheme leads to the following expression for the

intensity I :

$$I_{0_n} = k_{f_n} [H^*] \quad \dots (8)$$

$$I_0 = \sum_n I_{0_n} = k_{f_n} [H^*] \quad \dots (9)$$

$$\text{At equilibrium } d[H^*]/dt = 0 \quad \dots (10)$$

i.e.

$$k_a [H] = k_p [H^*] + k_s [H^*] [H] \quad \dots$$

$$\therefore [H^*] = \frac{k_a [H]}{k_p + k_s [H]}$$

$$\therefore I_0 = \frac{k_p k_a [H]}{k_p + k_s [H]} \quad \dots (11)$$

and also

$$I_{0_n} = \frac{k_p k_a [H]}{k_p + k_s [H]} \quad \dots (12)$$

Taking inverse of the equation (12) we get :

$$\frac{1}{I_{0_n}} = \frac{k_p}{k_a k_{f_n} [H]} + \frac{k_s}{k_{f_n} k_a} \quad \dots (13)$$

Where

$[H]$ = concentration of the iodine molecule in the ground state.

$[H^*]$ = concentration of the iodine molecule in the 26th vibrational level of the excited state.

I_0 = total intensity of the fluorescence.

subscript n represents any other level of the excited state.

TABLE - I

DATA FOR THE OSMOTIC PRESSURE CONSTANTS (EXPRESSED IN MM.)

Sl. No.	Temp. (°C.)	Vapor Pressure (mm. Hg.) (a)	Concentration (Molar) (b)	1×10^4 (molar) Intensity	$\frac{1}{1 - x} \times 10^{-6}$	$\frac{1}{1 - x} \times 10^2$
1	0	0.0577	2.2203	8.5	0.4504	11.70
2	50	0.0575	5.3167	13.5	0.3050	7.40
3	100	0.0574	4.9964	18.5	0.2005	5.40
4	150	0.0572	7.5168	22.0	0.13309	4.524
5	200	0.0571	10.94603	25.5	0.0913	3.90
6	250	0.0570	16.41126	26.0	0.0609	3.819
7	300	0.0567	24.6095	31.0	0.0406	3.226

(a) From Appendix 1.

A plot of $\frac{1}{T_{10^{\text{m}}}}$ against $\frac{1}{[H]}$ yields an intercept/slope ratio equal to self quenching constant $\frac{k_s}{k_p}$. Here k_s is the rate constants for self quenching and k_p is the rate constant for fluorescence. The inverse of rate constant for fluorescence gives the radiative life-time of excited state. The radiative lifetime has been determined by Brewer, Berg, and Rosenblatt⁽⁸⁾. It was found that the mean radiative lifetime of the excited molecule of iodine in $v' = 25$ is equal to 7.2×10^{-7} sec.

From the plot of $\frac{1}{T_{10^{\text{m}}}}$ against $\frac{1}{[H]}$ the value of self quenching constant $\frac{k_s}{k_p}$ was found to be 2.1×10^5 liter per mole.

Since the rate constant for fluorescence k_p is given by the inverse of the radiative lifetime of excited molecule of iodine

$$\text{i.e. } k_p = \frac{1}{\tau} \quad \dots \quad (14)$$

$$\therefore k_p = 48. \times 10^{-11} \frac{\text{cm}^3}{\text{molecule sec.}}$$

Using the equation (3) for collision cross section for self quenching the σ_s^2 was found to be $68.2 \times 10^{-16} \text{ cm.}^2$

DATA FOR SELF QUENCHING CONSTANTS (EXPERIMENTAL)

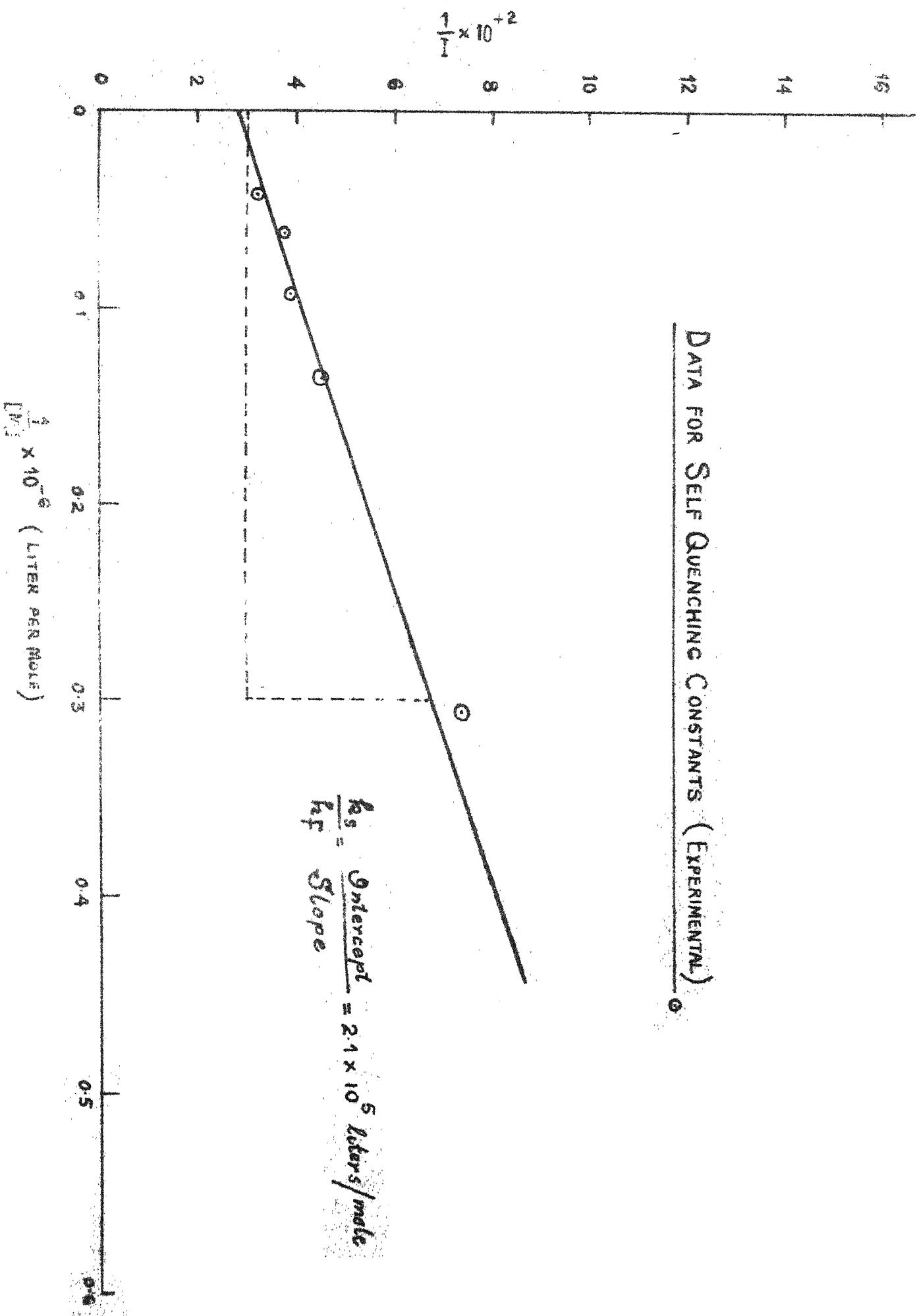


FIG. 5.

CONCLUSION

In this work the major part of the time was spent in setting up of the apparatus which includes a vacuum and an optical system.

A thermocouple gauge to measure pressures upto a micron, was included in the vacuum system. A liquid nitrogen trap was also enclosed between the thermocouple gauge and fluorescence cell to freeze down any of the vapor. By repeated pumping operations it was made sure that iodine vapor taken into the flask was pure and uncontaminated. Each run at a particular vapor pressure was repeated at least three times, so each point corresponds to an average of three runs. From the data obtained the self quenching constant of fluorescence and other kinetic parameters such as collision cross-section, collision frequency etc. were calculated. The results are in close agreement in the literature values (4, 5, 6, 10).

The problem was started with a view to measure and compare the relative reaction rates in a complex kinetic scheme. For this purpose it was the aim to measure the self quenching of fluorescence and quenching of fluorescence by foreign gases. Unfortunately due to several problems in the setting up of the apparatus and in obtaining a stable power, the work has been slowed down considerably. Hence the second part of the problem was not been attempted.

However, the results obtained on self quenching suggests that the apparatus and the experimental system is reliable and work can be continued on foreign gases. The whole mechanism

of quenching processes can be studied by using gases of widely differing molecular weight and dipole properties.

R E F E R E N C E S

1. Wood, R.W.
 - a) "Resonance Spectra of Iodine Vapor and Destruction by Gases of the Hg. Group", Phil. Mag., 22, 469, (1911).
 - b) "Resonance Spectrum of Iodine by Multiplex Excitation", Phil. Mag., 24, 673, (1912).
 - c) "The Time Interval Between Absorption and Emission of Light in Fluorescence", Proc. Roy. Soc., A 99, 362 (1921).
 - d) "Fluorescence and Photochemistry", Phil. Mag., 42, 757, (1922).
 - e) "The Fluorescence, Magnetic Rotation and Temperature Emission Spectrum of Iodine Vapor", Phil. Mag., 12, 329, (1906).
2. Wood, R.W. & J. Franck, "Transformation of Resonance Spectrum into a Band Spectrum by Presence of Helium", Phil. Mag. 21, 265, (1911).
3. Polanyi, J.C., "Quenching and Vibrational Energy Transfer of Excited Iodine", Canadian J. Chem. 36, 121, (1958).
4. Arnot, C. and McDowell, C.A., "Quenching of the Iodine Fluorescence Spectrum", Canadian J. Chem., 36, 114, (1958)
5. Arnot, C. and McDowell, C.A., "Quenching and Vibrational Energy Transfer of Excited Iodine Molecule", Canadian J., 36, 1322 (1958).
6. Brown, R.L. and Klemperer, W., "Energy Transfer in the Fluorescence of Iodine Excited by the Sodium D-Lines", J. Chem. Phys., 41, 3072 (1964).
7. Pringsheim, P., "Fluorescence and Phosphorescence", Interscience Publishers Inc., New York, (1949).

8. Brewer, L., Berg, R.A., and Rosenblatt, G., " Radiative Lifetime of Iodine Fluorescence ", J. Chem. Phys., 38, 1381 (1963).
9. Chutjian, A., Link, J.K., and Brewer, L., "Measurement of Lifetime and Quenching Cross-sections of the B State of Iodine ", J. Chem. Phys., 46, 2666, (1967).
10. Jeffrey, I., Steinfield & William Kelisperer, " Energy Transfer Processes in Monochromatically Excited Iodine Molecule - I Experimental Results ", J. Chem. Phys., 42, 3475 (1965).
11. Lois Mathieson & Rees, A.L.G., " Electronic States and Potential Energy Diagram of Iodine Molecule ", J. Chem. Phys., 25, 753, (1956).
12. Lenz, W., " Theory of Band Spectra in Relation to Molecular Structure", Ber. Physik. Ges., 21, 632 (1919)
C.A., 14, 2296(1920)
13. a-Kratzer, A., " The Theory of Band Spectra " Z. Physik, 26, 40 (1924), C.A., 18, 3541 (1924).
b-Mecke, R., " The Band Spectrum of Iodine ", Ann. Physik, 71, 104 (1923), C.A., 17, 2994 (1923).
14. Loomis, F.V., " New Series in Spectrum of Fluorescent Iodine", Phys. Rev., 29, 355, (1927).
15. Rabinowitch, E. & Wood, W.C., " Dissociation of Excited Iodine Molecule ", J.Chem. Phys., 4, 355, (1936).
16. Turner, L.A., " Optional Dissociation of Iodine and Enhancement of Predissociation by Collisions ", Phys. Rev., 41, 627, (1932).
17. Mulliken, R.S., " Halogen Molecule Spectra ", II Internal Relations and Relative Intensities in the Long Wave-length Spectra ", Phys. Rev. 57, 500, (1940).

18. Mulliken, R.S., "The Interpretation of Band Spectra", Revs. Modern Phys., 4, 1, (1932).
19. Zener, C. Proc. Roy. Soc. (London), 140, 660, (1933).
20. Jeffrey, I. Steinfeld, "Wavelength Dependence of Quenching of Iodine Fluorescence", J. Chem. Phys., 44, 2740 (1966).
21. Louis, J. Gillespie and Lewis, H.D. Fraser, "The Normal Vapor Pressure of Crystalline Iodine", J. Am. Chem. Soc., 58, 2260, (1936).

APPENDIX - I

NORMAL VAPOR PRESSURE OF SOLID IODINE IN
MM. OF MERCURY

<u>t°C.</u>	<u>P (mm. of Hg.)</u>
0	0.0507
10	0.0814
20	0.201
25	0.309
30	0.467
40	1.027
50	2.144
60	4.276
70	8.175
80	15.04
90	26.73
100	46.97
110	76.76
114.15 (mp.)	94.14